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Poly(enaminonitriles) contain structural elements which have sufficient hydrogen-bonding capability that these polymers can form compatible blends by solution casting with polymers such as poly(ethylene oxide) (partially miscible), poly(ethyl oxazoline) and poly(4-vinyl pyridine) (miscible over the whole concentration range). The properties of these membranes are described and their potential use as separation membranes is considered.

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"Blends of Poly(enaminonitriles)"

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J. A. Moore and Ji-Heung Kim

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BLENDS OF POLY(ENAMINONITRILES)

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INTRODUCTION

Polyenaminonitriles (PEANs) are novel, high molecular weight, film-forming polymers which have excellent thermal stability and good mechanical properties. This polymer exhibits an exciting array of physical properties and chemical behavior. In this paper, we report lower critical solution temperature (LCST) behavior of PEAN in polyether solvents and its ability to form blends with several polymers, especially good proton-acceptors such as poly(vinyl pyridine), poly(ethylene oxide), poly(ethyl oxazoline) and poly(vinyl pyrrolidone).

Various authors have commented on the potential usefulness of miscible blends.[1,2,3] Interest is growing in the use of blends as barrier materials and as membranes for separation processes. The observation of a single concentration dependent glass transition temperature (Tg) between the Tg of the component polymers is usually taken as evidence of miscibility of the blend of polymers, even if one or both of them crystallize. Hydrogen bonding, acid-base and/or dipole-dipole type interactions are mainly responsible for the observed polymer-polymer miscibility. The variation of T_g with composition is reported here as determined by differential scanning calorimetry(DSC). Fourier-transform infrared(FT-IR) spectrometry was used to study the specific hydrogen bonding interactions involved in these blend systems.

EXPERIMENTAL

Materials

Three different polyenaminonitriles were synthesized by using the typical procedure we have developed.[4] Their structures and characteristics are shown in Table 1. Poly(4-vinyl pyridine) (P4VP) and poly(2-vinyl pyridine) (P2VP) were obtained from Polyscience, Inc., with molecular weights of 50,000 and 40,000 Daltons, respectively, and used without purification. Poly(ethyl oxazoline) (PEOX) with a molecular weight of 200,000 Daltons was generally provided by the Dow Chemical Co., and purified by precipitation of a MEK solution into a large volume of n-hexane and dried under vacuum at 80 °C for 2 days. PEO with average molecular weight 100,000 Daltons, was purchased from Aldrich Chemical Co.. Poly(N-vinyl pyrrolidone) (PNVP) from GAF Chemicals Co., PVP K-90, was used.

Cloud Point Measurements

Cloud points of PEAN in glyme solvents were measured by a scattering method using a laser source or could be detected easily by visual observation. Polymer solutions were placed in stoppered test tubes immersed in an oil bath which was heated at a rate of approximately 1 °C/min. The temperature at which the scattering intensity increased abruptly was taken as the cloud point. A typical scattering intensity vs. temperature curve is shown in Figure 1. Duplicate measurements were reproducible to ±0.5 °C.

Blend Film Preparation

Blends were prepared by solution casting from DMF as the mutual solvent. The total polymer concentration in the solution was 3-4 %. The blended samples were cast on aluminum pans or glass plates and evaporated at 50 °C under nitrogen flow. The cast films were dried at 80 °C in a vacuum oven for 2 days and kept in a desiccator prior to measurement. The samples for FT-IR analysis were cast on a NaCl plate using the same drying procedure.

DSC Measurements

Thermal analysis studies were performed on a Perkin-Elmer System 7 differential scanning calorimeter interfaced with a Perkin-Elmer Model 7500 computer. A heating rate of 20K/min was used in all measurements. Sample sizes ranged from 5 to 10 mg. The glass transition temperature was taken as the midpoint of the heat capacity change. Usually the first scan did not show Tg clearly bacause traces of solvent remained in the film. The Tg values from the second run are reported.

FT-IR And NMR

Fourier transform infrared(FT-IR) spectra were recorded on a Perkin-Elmer Model 1800 spectrometer at a resolution of 2 cm^{-1}. A minimum of 64 scans were averaged and the spectra stored on a magnetic disc. NMR spectra were recorded on a Varian Model XL-200 spectrometer.

RESULTS AND DISCUSSION

Lower Critical Solution Temperature (LCST) Behavior of PEAN in Polyether Solvent

PEAN showed LCST behavior in polyether solvents, and this behavior looks quite general in almost all the PEANs with different structure synthesized in our group. The cloud point curve of 1,3 PEAN in a series of glyme solvents are shown in Figure 2. As the number of oxyethylene repeating unit increases in the solvent, $CH_3O-(CH_2CH_2O)_N-CH_3$, the cloud point increases and then tends to level at higher value of N. The same trend were observed in the cloud point data of two other polymers. Their cloud point curves are

shown in Figure 3. The phase separation process was totally reversible in 1,3 PEAN and PEAN 2. On the contrary, 1,4 PEAN showed irreversibility, in other words, this polymer precipitated from solution and did not redissolve. It seems that this behavior arises from the more ordered structure of para-linked 1,4 PEAN that might induce the polymer chain to orient and pack regularly to give a less soluble macrostructure during the phase separation process. The cloud point temperature is related to the structure of the polymers. Polymers with more flexible chains exhibit better solubility and higher cloud points. LCST behavior and increasing solubility in higher glyme solvents implies the possiblility that PEAN may form blends with high molecular weight PEO.

P4VP/ PEAN Blend

Blends of P4VP with 1,3 PEAN, 1,4 PEAN and PEAN 2 are miscible over the entire composition range. Films cast from mixtures of the two polymers in DMF are completely transparent and each blend exhibits a single Tg which varies smoothly with composition between the Tg values of the two component polymers. The Tg-composition curve of P4VP/1,3 PEAN blend is shown in Figure 4.

FT-IR spectra of the P4VP/1,3 PEAN system suggest that hydrogen bonding interactions are involved in stabilizing these blends.
Figure 5 shows representative scale-expanded infrared spectra of the N-H stretching region of pure 1,3 PEAN and its blends. As the concentration of P4VP is increased, the N-H band originally centered at 3240 cm^{-1} shifts to lower frequency around 3190 cm^{-1}. NMR spectra of model compound, 1,3-bis[2,2-dicyano-1-(4-phenoxy phenyl)amino vinyl] benzene, also suggest very strong interaction of the -NH proton with pyridine. The NH proton peak originally at 9.96 ppm in aceton shifts downfield more and more and undergo peak broadening as pyridine-d5 is added to the solution in NMR tube.

In contrast to the observed miscibility between 1,3 PEAN and P4VP, P2VP was found to form immiscible blends with 1,3 PEAN. Figure 6 shows DSC traces of this blend system. Only blend film composed of 10 wt% P2VP was clear. From 20 wt% P2VP on, the films began to be translucent and became completely opaque at higher concentrations of P2VP. Two clear separate Tg indicate the immiscibility of this system. Probably more sterically hindered surroundings compared to the P4VP/1,3 PEAN system must prevent strong interactions between these two polymers. FT-IR of the blend also suggests much reduced interaction of NH protons. Very small shifts and shape change were observed for the NH band compared to the P4VP/1,3PEAN blend system. In relation to this result, it seemed useful to check the solubility of 1,3 PEAN in 2-picoline(2-methyl pyridine) and 2,6-lutidine(2,6-dimethyl pyridine). The polymer was soluble in both solvents. But, interestingly, a polymer solution in 2,6-lutidine showed LCST behavior with a cloud point around 60 °C, and this process was totally reversible. 2-Picoline solution didn't show any phase separation up to the boiling temperature of the solvent.

PEOX/1,3 PEAN Blend

Poly(ethyl oxazoline) is a new water soluble polymer. Many miscible blends have been reported with this polymer. PEOx is considered to be a good hydrogen bonding acceptor because of the slightly 'basic' nature of the substituted amide structure. It is expected, therefore, to form miscible blends with polyenaminonitriles. The Tg-composition curve is shown in Figure 7. A single Tg over the whole composition range indicates complete miscibility between these two polymers. IR spectra of blends suggest strong hydrogen bonding interactions as evidenced by a shift of the NH stretching band region shown in Figure 5.

PNVP/1,3 PEAN Blend

Poly(N-vinyl pyrrolidone) which contains a substituted amide group similar in structure to that in PEOX should also be miscible with PEAN. The Tg-composition curve is shown in Figure 8. Composition dependent single Tg over the entire range indicates complete miscibility of these polymers and almost same pattern of NH shift was observed by IR spectroscopy.

PEO/1,3 PEAN Blend

PEO was expected to be miscible with PEAN because PEO is one of polymers that are relatively weakly self-associated but contain sites, the oxygen atoms, which are capable of forming a strong interaction (hydrogen bonding in this case) with PEAN. Further, the solubility property of PEAN in polyether solvents suggests strong interaction between these two polymers. However, the phase behavior of PEO/1,3 PEAN blend does not seem to be simple to explain. Crystallization of PEO in the blend and phase separation at certain compositions and temperatures seems to make thermal analysis more complicated. 10, 20, 30, 50 wt% PEO blend films cast from DMF were clear visually. But the 30% and 50% blend samples showed small, broad melting exotherm around 55-60 °C indicating development of PEO crystalline phases. Another interesting fact is that phase separation was observed clearly from a 50% blend sample on a hot stage optical microscope at around 150-160 °C. When the sample film was cooled, the turbid film became clear again visually, but separated PEO spheres in the continuous matrix were clear through the microscope. Probably the reverse process is kinetically very slow because of the low mobility of these high Tg mixtures. More experimental data is needed to explain this behavior and is currently being collected.

SUMMARY : PEAN forms miscible blends PEAN forms with several commercial polymers described above. It is noteworthy that PEO, PEOX and PNVP used in our blends are water soluble polymers. The excellent thermal stability and good mechanical properties of PEAN polymers coupled with their high affinity for such water soluble and/or polar polymers suggest that such blends may find application as membrane materials.
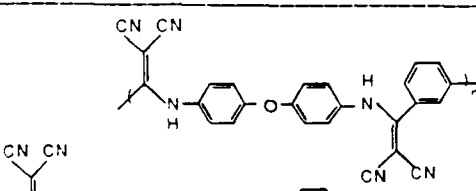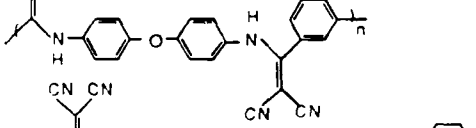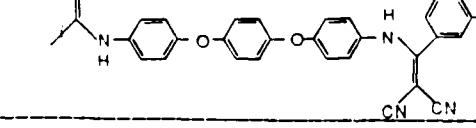
REFERENCES

1. O. Olabisi, L. M. Robeson, and M. T. Shaw, Polymer-Polymer Miscibility, Academic Press, New York, 1979
2. K. Solc, Polymer Compatibility and Incompatibility, MMI Press, Midland, 1982
3. D. R. Paul and J. W. Barlow, J. Macromol. Sci. -Rev. Macromol. Chem. C18, 109 (1980)
4. J. A. Moore and Douglas R. Robello, Macromolecules, 1989, 22, 1084.

ACKNOWLEDGMENT

Table 1.

	Structure	intrinsic viscosity*
1.3 PEAN		0.37
1.4 PEAN		0.40
PEAN 2		0.51

* Viscosity wes measured with a Cannon-Ubbelohde viscometer at 25 °C in DMF.

Figure 1.

Scattering Intensity vs. Temperature

cloud point of 1,3PEAN in glyme solvent

Figure 2.

Concentration, 0.2 g/10cc

$CH_3O (CH_2CH_2O)_N CH_3$

**Cloud Point of Three Different PEAN
in Glyme Solvent**

Figure 3.

PEAN2
1,3PEAN
1,4PEAN

$CH_3O-(-CH_2CH_2O-)_N-CH_3$

Figure 4.

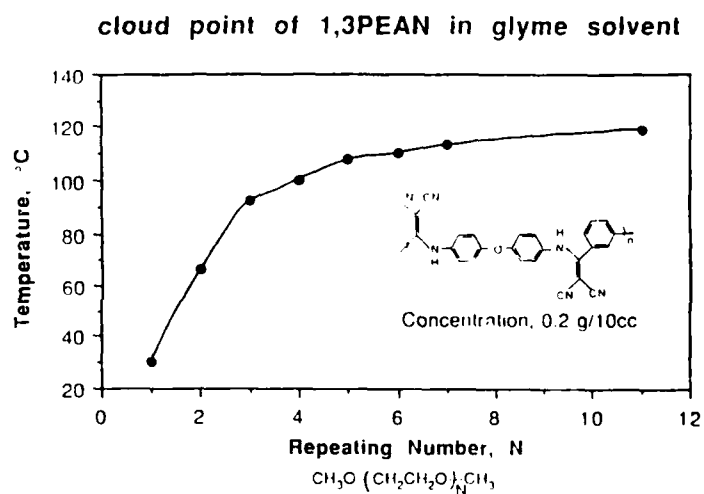**1,3 PEAN/P4VP Blend**
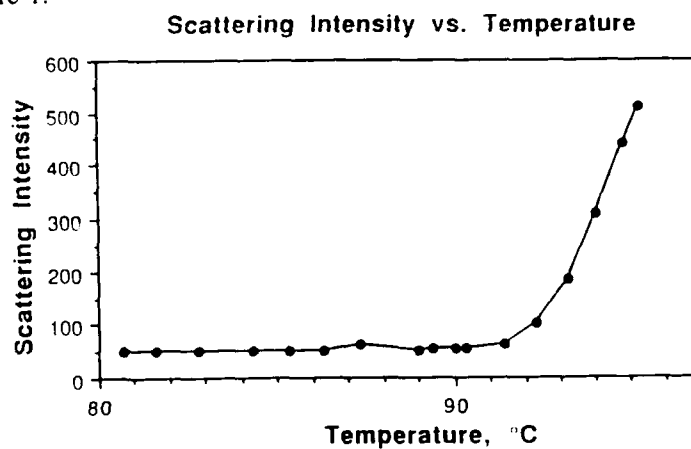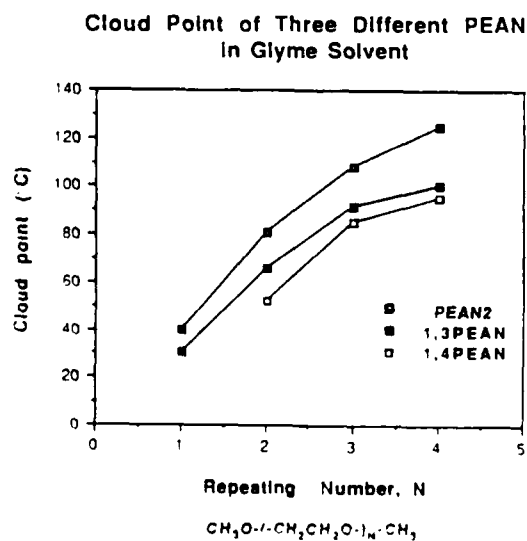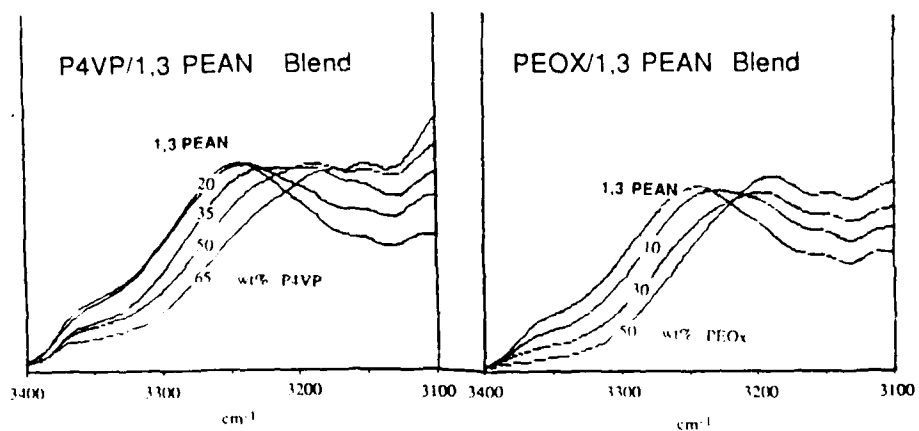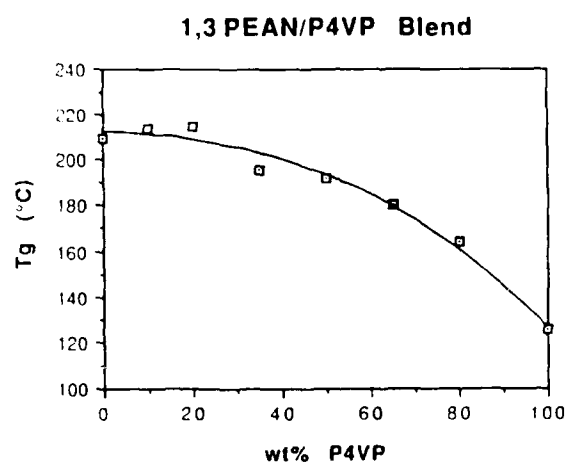

P4VP/1,3 PEAN Blend   **PEOX/1,3 PEAN Blend**

Figure 5.   The N-H stretching region of the FT-IR spectra
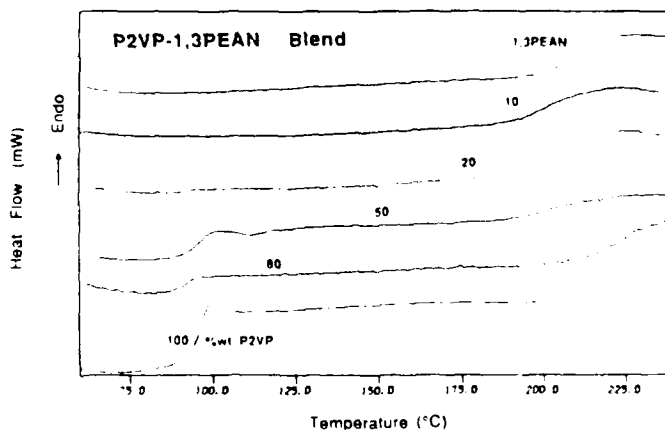
Figure 6.   DSC of P2VP/1,3 PEAN BLEND
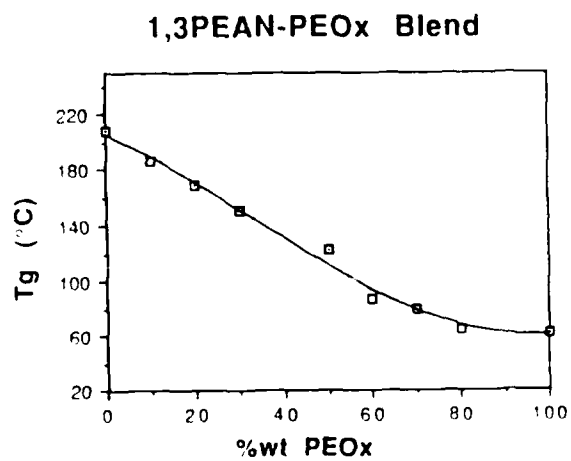
1,3PEAN-PEOx Blend

Figure 7.

PNVP/1,3PEAN Blend

Figure 8.